The importance of orientation

- For **unoriented** samples there exists a “universal curve” plotting Modulus vs. Yield Strength. High modulus implies high yield strength.

- Conversely it's difficult to move off this line. It's 'impossible' to find a material with a low modulus and a high tensile strength.
• Modulus of “cold drawn” material increases as a function of draw or deformation ratio. Different relationship for different polymers. Shown is POM.

• Many polymers have a "natural" draw ratio. Polymers tend to deform so that at some temperature, draw ratio is relatively independent of drawing conditions.

• To obtain a wide range of draw ratios we need to have a very wide range of drawing conditions.
• Similar effect of draw ratio on Yield strength. Shown below is the effect on Nylon yield after uniaxial or biaxial drawing, and rolling.

- Deformation ratios >1, sample tested in the draw direction; <1, sample was tested perpendicular to the draw direction.
• Both modulus and yield strength increase as draw ratio increases. However, draw ratio affects modulus and yield/tensile strength differently.

• In particular, for many polymers there appears to be a greater effect of draw ratio on yield or tensile strength. Modulus doesn't continue to increase as draw ratio increases but may either plateau out or show a change in slope.
The net result is a complex relationship between modulus and strength in drawn materials.
Orientation

• Polymer chains are oriented during processing. Such orientation may be deliberate, and lead to property improvement, or it may not.

• Orientation does not imply crystallinity. Polymers can be amorphous and yet oriented.
• Herman's orientation function \( f \) is simply a mathematical construction that allows us to describe the degree or extent of orientation of the chain axis relative to some other axis of interest.

\[
f = \frac{3 \cos^2 \theta - 1}{2}
\]

• Herman's orientation function '\( f \)' has the properties that, relative to the direction of interest, if 'on average' the chain axis is:-

- completely aligned \( f = 1 \)
- randomly oriented \( f = 0 \)
- perpendicular \( f = -0.5 \)
• Physical properties are assumed to be a linear function of 'f' and the intrinsic property, and are additive based on the amount of each component.
Stretch Direction

- Aligned Parallel (fc = 1)
  - Intrinsic Birefringence = Δ°c

- Aligned Parallel (fam = 1)
  - Intrinsic Birefringence = Δ°am

- Orientation function fc ≠ 1
  - Birefringence = fc. Δ°c

- Orientation function fam ≠ 1
  - Birefringence = fam. Δ°am

Measured Birefringence (Δt) is

Δt = β. fc. Δ°c + (1 - β). fam. Δ°am

β (1 - β)
• 'f' helps to define chain orientation relative to some direction of interest, we pick directions of interest that are important relative to processing.

• For fiber production the direction of interest is the fiber axis; the fiber is loaded along this axis.

• For more 3 dimensional objects we usually select one of three orthogonal axes:-

• Note there may be simple relationships between 'f' as measured relative to one direction of interest, say TD and some other 'f' measured relative to another direction of interest say MD.
• Alternative ways of defining orientation have been used:

\[ \text{Draw or Orient} \]

\[ L_x^o \rightarrow L_x \]

• The draw ratio (R) is defined as:

\[ R = \frac{L_x}{L_x^o} \]

• For 'cold drawn' polymers R and f are related as:

\[ f \approx \log R \]
• 'Cold drawn' implies drawing polymer in the solid state below Tm; it introduces lots of orientation.

• In melt processing, particularly fiber or film production, draw ratio is defined similarly and draw ratios of 50 to 100 are not uncommon.

• However, after being oriented a melt tends to 'relax' losing some of the imposed orientation before it solidifies.

• In fiber production, additional cold drawing is used to give better polymer chain orientation.
Review of X-ray diffraction, to determine the orientation of chains in a crystal lattice

- Unit Cell - the smallest volume the crystal can be divided into and still retain the basic crystal structure. Analogous to atom/element.
• Unit cell dimensions are \( a, b \) and \( c \), measured along the \( X, Y \) and \( Z \) directions respectively.

• Miller Indices - method for identifying planes (or families of planes) in the crystal. Recipe:-

Plane cuts \( X, Y \) and \( Z \), in units of \( a, b \) or \( c \), at :-

\[ 1, 0.5, \infty \]

Take reciprocal \( 1, 2, 0 \)
• Poles or Normals - that direction that cuts a particular plane at 90°.

• For diffraction the **incident, normal and diffracted beams** must be in the same plane.

• Bragg equation
  
  \[ n\lambda = 2d \sin\theta \]

  Diffraction Angle (2\(\theta\))
• Use film as a detector of X-rays

- A diffraction spot on the film implies a set of planes inclined at the correct $\varnothing$ to the incident beam.
• With enough planes in the sample that are:-
  a) inclined at the correct $\varnothing$, and yet
  b) rotated about the incident beam

• We see a diffraction circle; this classic **powder pattern** shows **random orientation**.
The problem

- Note that in the previous example, diffraction only arises from planes that are inclined at the correct $\varnothing$ to the main beam. For diffraction, planes must be inclined at the correct $\varnothing$.

- Consider an example where the planes of interest are all lying in some sample plane (TD/N plane).
• No matter along which major axis you send the incident beam, you never get diffraction.

• The X-ray diffraction experiment only 'samples' those planes that are inclined at the correct $\varnothing$ angle to the main beam.
The solution

• Basically, rotate the sample.

• Set the diffractometer so incident and detector are at the correct 2Ø for some set of planes.

• Start with the incident beam along one of the major axes (MD) and rotate the sample about TD, so that N sweeps through an angle β.
- Record intensity as measured at the detector as a function of angle $\beta$.

- When the maximum number of planes are inclined $\varnothing$ to the incident beam you'll see a maximum in intensity vs. $\beta$. Distribution in $\beta$ models the distribution of plane inclinations.
• Determining plane positions is now all geometry:
  * suppose the correct $\varnothing$ for a set of planes is $28^\circ$
  * suppose the maximum in the $\beta$ plot is at $17^\circ$

• This means I had to rotate planes by $17^\circ$ before they were at $28^\circ$ to the main incident beam.
• Therefore the original position of the planes was either, $28 - 17 = 11^\circ$ to the incident beam
or $90 - 11 = 79^\circ$ to the original N position.

• Since the poles to the planes are at $90^\circ$ to the planes this means that the poles to these planes are lying $\approx 11^\circ$ from the original N direction.

• All the above will work assuming that planes are parallel to TD (in this case). Since there is no guarantee of this orientation, we need to sample ALL possible angles/orientations. Such operations produce lots of data that needs presenting in an understandable manner.
Data presentation: Pole Figures

- Draw a sphere with the sample in the center and showing TD, MD and N (or ND)

- Instead of reporting planes that we are interested in, we show their poles. Poles are derived from the series of X-ray experiments described earlier.

- Poles are projected onto the surface of the sphere.
• In practice, instead of a single spot we may see a band of high intensity indicating a high concentration of poles at a particular location.

• As an exercise describe both the distribution of **poles** and the distribution of **planes** as indicated by the pole figures shown below.
• Conventionally, in X-ray studies, the polymer chain axis is usually reported as lying along the 'Z' or 'c' axis. So, if we can determine the pole figure for 001 planes we will then also know the distribution of 'c' axes, and therefore, the distribution of polymer chain axes.

• If we know the chain axis distribution, we can work out Herman's orientation function for polymer chains that are in crystalline regions.
• So far we have focused on a single set of planes and primarily 001 planes, that are used to show the orientation of polymer chain axes.

• To completely describe orientation we need to know orientation of other crystallographic axes relative to sample process axes.

• We need to find the distribution of two orthogonal crystallographic axes relative to TD, MD and N.
• Such a requirement implies that we need to determine pole figures for two of the following sets of planes (see below).

```
  TD  MD  ND
  100  "a"

  TD  MD  ND
  010  "b"

  TD  MD  ND
  001  "c"
```

• Based on discussions so far this requirement simply means we first set-up the X-ray diffractometer so that 2Ø for the 001 is satisfied.

• After completing these experiments the diffractometer is reconfigured for the correct 2Ø for either the 100 or 010 planes.
• These requirements may appear trivial, however, there is a problem. Because of the way chains are packed within the crystal, it may be that the crystal doesn't have the required 100, 010 or 001 reflections. (The electron density distribution is such that these planes don't have sufficient contrast to permit diffraction.)

• In that case it is necessary to deduce the distribution of the primary crystallographic axes from any reflections that do exist.

• For example, the two strongest reflections in PE are from 110 and 200 planes. With other weaker reflections one can deduce, using rather complex and messy geometry a, b and c axis distributions.